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Dynamic oxidation and protection of the PAN pre-oxidized fiber C/C composites

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ABSTRACT

Pre-oxidized fibers as reinforcement are candidates for reducing the overall cost of C/C composites with superior properties. This study investigated the dynamic oxidation and protection of the pre-oxidized fiber C/C composites (Pr-Ox-C-C). According to the Arrhenius equation, the oxidation kinetics of the Pr-Ox-C-C consisted of two different oxidation mechanism with the transition point was at about 700 °C. Scanning electron microscopy investigation showed that oxidation initiated from the fiber/matrix interface of composites, whereas the matrix carbon was easily oxidized. To improve the anti-oxidant properties of Pr-Ox-C-C, a ceramic powder-modified organic silicone resin/ZrB_2-SiC coating was prepared by the slurry method. The coated samples were subjected to isothermal oxidation for 320 h at 700 °C, 800 °C, 900 °C, 1000 °C and 1100 °C with incurred weight losses of − 1.6%, 0.77%, − 1.28%, 0.68% and 1.19%, respectively. After 110 cycles of thermal shock between 1100 °C and room temperature, a weight loss of 1.30% was obtained. The Arrhenius curve presented four different phases and mechanisms for coating oxidation kinetics. The excellent oxidation resistance properties of the prepared coating could be attributed to the inner layer which was able to form B_2O_3-Cr_2O_3-SiO_2 glass to cure cracks, and the ZrB_2-SiC outer layer that could provide protective oxides to reduce oxygen infiltration and to seal bubbles.

1. Introduction

Carbon/Carbon (C/C) composites refer to a kind of excellent thermal structure material with outstanding mechanical properties and corrosion resistance. In particular, under high-temperature conditions, C/C composites can maintain excellent mechanical properties. Therefore, C/C composites have been widely applied in hot components of aeronautics and astronautics [1–3]. However, these applications are limited by high cost, long processing time, and large energy consumption of reinforcement carbon fiber. To reduce the overall cost of C/C composites, pre-oxidized polyacrylonitrile-based (PAN) fibers are applied as the reinforcement to replace carbon fibers [4,5]. Pre-oxidized PAN fibers are intermediate products of carbon fibers, which exhibit high yield and superior mechanical properties; these fibers can be prepared by stretching PAN precursor fibers during 200–300 °C in an oxidation atmosphere [5,6]. Previous studies have indicated that the desired comprehensive performance of Pr-Ox-C-C can be achieved by controlling the microstructure of carbon matrix and/or combination of control fibers and the matrix [7,8]. Studies show that pre-oxidized PAN fibers can be used as an ideal substitute for the preparation of C/C composites, which are widely applied to aircraft braking devices [4–6]. Whereas, similar to carbon fiber-reinforced carbon matrix materials, when exposed to oxidizing environment above 500 °C, Pr-Ox-C-C will react with oxygen, and their original excellent properties will decline rapidly [9]. A significant number of literature discussed oxidation of C/C materials [10–15], pprevious studies have concluded that oxidation mechanism and microstructure of carbon materials depend on the type of pyrolytic carbon and fiber [16]. The type of pyrolytic carbon affects the rate of surface oxidation. The highly crystallized carbon and the carbon with high graphitization manifest better resistance to oxidation [17]. Reinforced fibers affect the path of oxygen diffusion, with oxygen commonly diffused into the interface between fiber and matrix along the fiber axial [11]. PAN fibers made from polyacrylonitrile have better internal oxidation resistance. The reason is that the internal of PAN fibers have higher crystallinity than the edge portion [17]. Nevertheless, a limited number of research studied oxidative behavior and kinetics of Pr-Ox-C-C. The oxidation behavior of Pr-Ox-C-C differs from that of C/C composites made using carbon fibers owing to the different texture types and microstructure of fiber and matrix [4,5,18].

The oxidation-resistant coating is the most common solution to solve the problem that Pr-Ox-C-C are susceptible to severe oxidation. Several methods can be applied to prepare protective coating with good performance, such as chemical vapor deposition [19], pack cementation [20], electrophoretic deposition [21], sol-gel method [22] and

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slurry coating method [23]. Noted that, slurry process owns many advantages, like simple procedure, low cost, high preparation efficiency, high practicability and controllability of coating thickness. Specifically, the slurry method can be applied to preparation of complex surface component coatings. Li Jun et al. [3] reported a SiC-B_4C/SiC/SiO_2 gradient multilayer coating prepared by pack cementation and slurry technique. Results show that the coating exhibite oxidation protective ability for C/C composites among 500–1500 °C. Using the slurry method, Xiang Yang et al. [24] developed a ZrB_2-SiC outer layer coating which was painted on the C/SiC composites with SiC coating. After oxidation at 1500 °C for 2 h, results show that weight loss of SiC-coated samples reach 4.6%, and that of the samples with ZrB_2-SiC/SiC multilayer coating totaled 0.4%. However, the said researchers used pack cementation to prepare the inner layer, leading to an extremely high preparation temperature. To reduce preparation temperature and to improve preparation efficiency, we prepared the both inner and outer layers of the proposed composite coating by the slurry method. The inner layer mainly consisted of BC_4 and SiO_2 ceramic powder-modified high-temperature organic silicon resin, and the outer barrier layer consisted of ZrB_2-SiC. The proposed self-healing coating system could improve oxidation resistance of composite materials below 1200 °C. B_4C possesses the characteristic of excellent oxidation resistance in the intermediate temperature range because it is oxidized to form a flowing glass phase B_2O_3, which can heal the micropores and microcracks produced during preparation and oxidation [3]. However, the susceptibility of B_2O_3 to volatile gasification at elevated temperatures limits its application [25]. Therefore, this study introduced BC_4 and SiO_2 ceramic powders into high-temperature silicone resin as the inner coating to solve the volatile problem of B_2O_3. Organic silicon resin is inexpensive, easy to paste, and exhibits good compatibility with carbon substrates [3]. High-temperature organic silicone resin contains a chromium oxide (Cr_2O_3) component, and during oxidation, B_2O_3-SiO_2-Cr_2O_3 glass with stable phase structure forms through the combination of B_2O_3, SiO_2 and organic silicone resin. ZrB_2 possesses excellent characteristics, such as low density, high melting point, and good thermal shock resistance. The ZrB_2/SiC outer layer can form Zr-Si-O glass at low vapor pressure and high temperatures [26], and can serve as an oxidation barrier to prevent evaporation and consumption of the inner layer coating.

This paper presents the results of a study on oxidation behavior and kinetics of C/C composites using pre-oxidized PAN fibers. A new multilayer coating system was developed, using modified high-temperature organic silicon resin/ZrB_2-SiC, which was coated on the Pr-Ox-C-C prepared by the slurry method. With respect to oxidation resistance, performance and anti-oxidation mechanism of the two-layer coatings were also investigated.

2. Experimental

2.1. Specimen preparation

The three-dimensional needle-punched Pr-Ox-C-C used in this study were fabricated using rapid diffusion chemical vapor infiltration (CVI) technology [27], with preformed PAN-based pre-oxidized fibers (Tuozhan Company, Yantai, China) as reinforcement, natural gas and dimethylmethane as matrix precursor [28]. Preforms were prepared by needling and punching the layers (0° and 90°) of non-woven long-fiber cloth and short-cut fiber web. Details of this processing step have been reported elsewhere [28]. After densification, bulk Pr-Ox-C-C was cut into $10 \times 10 \times 10\ mm^3$ standard samples with a density of $1.72\ g/cm^3$. All specimens were manually polished, then ultrasonicated with anhydrous ethanol, and dried at 373 K for 2 h.

2.2. Coating preparation

Three types of coatings was prepared: (NO. 1) ZrB_2/SiC single protective coating; (NO. 2) ceramic powder-modified high-temperature organic silicon resin coating; and (NO. 3) duplex coatings which consisted of ceramic powder-modified high-temperature organic silicon resin inner layer and ZrB_2/SiC outer layer.

ZrB_2/SiC (NO. 1) single coating was prepared by slurry brushing. The precursors for preparing NO. 1 coating included the following: 30–40 wt% ZrB_2 powders (325 mesh), 10–20 wt% SiC (320 mesh), and 40–60 wt% polycarbosilane (PCS)/xylene solution. The precursors were thoroughly mixed and pasted on previous specimens. After completion of the foregoing operation, the specimens were dried at 120 °C for 2 h, placed in an electric furnace, and heated in argon atmosphere during 900–1100 °C for 1 h. The slurry method was also used to produce NO. 2 single coating. NO. 2 coating layer comprised high-temperature heat-resistant organic silicon resin (Xi’an Jingjian Paint Co., LTD) modified by ceramic powders. The NO. 2 coating consisted of 10–15 wt% B_4C (400 mesh), 15–20 wt% SiO_2 (800 mesh), 5–10 wt% Al_2O_3 (300 mesh), and 55–70 wt% high-temperature organic silicon resin. Preparation process of the NO. 2 coating was as follows: the powders were milled for 5 h and mixed with organic silicon resin evenly. The specimens pasted with the slurry were cured at 200 °C for 1 h and finally placed them in an electric furnace filled with argon at 900 °C for 2 h. Preparation of NO. 3 coating was as follows: First, the ceramic powder-modified high-temperature organic silicon resin coating was applied on the Pr-Ox-C-C samples, which acted as the inner layer. Then, ZrB_2/SiC coating as the outer layer was thoroughly mixed and pasted on previous specimens.

2.3. Oxidation tests

Oxidation measurements of PAN-based pre-oxidized fiber-reinforced CVI carbon composites were conducted using a Metter Toledo Star TGA/SDTA 851. In this study, oxidation performance of uncoated Pr-Ox-C-C specimens and coated Pr-Ox-C-C samples were carried out in static air by thermogravimetric analysis (TGA). The former one were heated from room temperature to 900 °C at a heating rate of 10 °C/min, and the latter one were analyzed from room temperature to 1300 ℃ at a heating rate of 10 °C/min. The coated and uncoated specimens were subjected to isothermal oxidation tests in static air. Oxidization of uncoated and coated specimens was implemented under the temperatures of 600–800 °C (uncoated specimens at 600 °C, 650 °C, 700 °C, 750 °C and 800 °C) and 700–1100 °C (coated specimens at 700 °C, 800 °C, 900 °C, 1000 °C and 1100 °C), respectively. Masses of specimens were determined with a precision analytical balance (Model CPA225D, Germany ± 0. 1 mg). Weight change rate (W) of the specimens could be obtained by the following formula:

$$W\% = (m_0 - m_t)/m_0 \times 100\% \qquad (1)$$

where $m_0 and m_t$ are the weights of samples before and after oxidation, respectively.

Thermal shock tests were performed as follows. The samples were loaded into the tube furnace as temperature reached the required temperature (1100 °C). After 2 min, the samples were removed from the furnace, allowed to cool at room temperature for 3 min, weighed, and returned to the furnace. Afterwards, the above test procedures were repeated.

2.4. Characterization

This study investigated the oxidation process and morphology of as-prepared coating and Pr-Ox-C-C. Oxidation and morphology were characterized with a scanning electron microscope (SEM) (HITACHI S-4800) equipped with an energy dispersive spectroscope (EDS). The phase structure of the coatings was measured by X-ray diffraction (XRD; D/Max 2500PC, Rigaku, Japan).